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(58) Field of search

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(54) Process for minimizing color formation during base catalyzed ethoxylation of 2-hydroxyethylamines

(57) A process for minimizing color formation during ethoxylation of 2-hydroxyethylamines in the presence of a base catalyst is disclosed. The 2-hydroxyethylamines are selected from monoamines, diamines, polyamines and amine polymers. The 2-hydroxyethylamine is reacted with ethylene oxide in the presence of base and in the presence of a color reducing borohydride.

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SPECIFICATION

Process for minimizing color formation during base catalyzed ethoxylation of 2-hydroxyethylamines

5

Technical Field

The present application relates to minimizing color formation during the ethoxylation of 2-hydroxyethylamines in the presence of a base catalyst.

10 Ethoxylated amines have a wide variety of uses such as surface active agents, emulsifiers and textile aids. Of particular interest to the present application are those ethoxylated amines useful in detergent compositions. For example, U.S. Application Serial No. 452,646 to J. M. Vander Meer filed December 23, 1982, discloses detergent compositions which contain water-soluble ethoxylated amines having clay soil removal/anti-redeposition properties. These compounds are selected from ethoxylated monoamines, ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof.

15 The ethoxylated compounds of the Vander Meer application can be prepared by a two step process. For the diamines, polyamines, and amine polymers such as the polyalkyleneamines and polyalkyleneimines, there is preferably an initial step of condensing sufficient ethylene oxide with the amine to provide 2-hydroxyethyl groups at each reactive site, i.e. at each reactive hydrogen of each amino group. This initial step can be omitted by starting with a 2-hydroxyethylamine such as triethanolamine. In the second step, an appropriate amount of ethylene oxide is condensed with these 2-hydroxyethylamines in the presence of a base catalyst, such as an alkali metal (e.g., sodium, potassium) hydride or hydroxide to provide the respective ethoxylated amine. The total degree of ethoxylation (i.e. total moles of ethylene oxide) per reactive site is at least about 3, and is typically at least about 12.

25 A problem encountered during the base catalyzed ethoxylation of these 2-hydroxyethylamines is color formation. As ethylene oxide reacts with the 2-hydroxyethylamine, the ethoxylated amine formed darkens in color, usually to a reddish-brown. Most color formation occurs up to the point where 5 moles of ethylene oxide have been added per reactive site; subsequent ethoxylation dilutes the color formed. This color formation does not affect the performance of these ethoxylated amines with regard to clay soil removal/anti-redeposition properties. However, the color formed can affect the aesthetics (appearance) of the detergent composition, especially where dyes are added to provide a particular color. Such aesthetics can be particularly important for heavy-duty liquid detergent compositions.

35 While not wishing to be bound by theory, it is believed that color formation during base catalyzed ethoxylation of 2-hydroxyethylamines can be explained as follows: An additional mole of ethylene oxide condenses on the nitrogen atom of the 2-hydroxyethylamine to form the respective quaternary amine. This quaternary amine degrades by Hoffmann elimination in the presence of base and heat to form the respective 2-hydroxyethylamine and vinyl alcohol which tautomerizes to form acetaldehyde. This acetaldehyde undergoes Aldol condensation reactions to form polyolefinic aldehydes that are believed to be one of the color causing agents. See U.S. Patent 3,574,755 to McConnell et al., issued April 13, 1971, at column 2, line 37 to column 3, line 73, wherein this mechanism is proposed. Other unknown color agents formed as a result of base catalyzed ethoxylation of the 2-hydroxyethylamine or as a result of impurities in the 2-hydroxyethylamine may also be color causing agents. Whatever the source, it would be desirable to minimize such color formation, especially where the ethoxylated amine is to be used in a heavy-duty liquid detergent composition having a particular color.

BACKGROUND ART

50 U.S. Patent 3,200,155 to Kirkpatrick et al., issued August 10, 1965, discloses the preparation of N-polyoxyalkylated polyhexamethylene polyamines. The polyoxylation reaction is conducted in two stages. In the first stage, a polyhexamethylene polyamine is reacted with an alkylene oxide (e.g. ethylene oxide) in the absence of a catalyst to produce the respective N-hydroxyalkylated polyamine. In the second stage, this N-hydroxyalkylated polyamine is reacted with additional alkylene oxide (e.g. ethylene oxide) in the presence of an alkaline catalyst (e.g. KOH) to produce the N-polyoxyalkylated polyamine. Example 18 discloses an ethylene oxide adduct of bis-(hexamethylene)triamine formed by this 2-stage process.

55 U.S. Patent 3,168,569 to Matell, issued February 2, 1965, discloses that polyalkylene glycol derivatives prepared by reaction of an alkylene oxide such as ethylene oxide with an organic compound containing a reactive hydrogen atom, such as an amine, are discolored. Appreciable color reduction occurred when these discolored derivatives were contacted with complex borohydrides such as sodium or potassium borohydride. The borohydride can be included during preparation of the polyalkylene ether derivatives so that dark color in the product can be prevented. Examples 2 and 9 disclose the treatment of ethylene oxide condensation products of oleylamine with sodium borohydride. See also U.S. Patent 3,207,790 to Glew, issued

September 21, 1965, which discloses that the color of alkanolamines, such as triethanolamine, can be reduced by treatment with borohydride.

U.S. Patent 3,574,755 to McConnell et al., issued April 13, 1971, discloses that the reaction of N,N-bis(2-hydroxyethyl)-N-alkyl or alkenyl amines (or the respective alkyl or alkenyl trimethylenediamines) with ethylene oxide results in products which are usually dark colored. One of the proposed mechanisms for discoloration is the formation of acetaldehyde during this process. Discoloration is prevented by reaction of the alkyl or alkenyl amine (or alkyl or alkenyl trimethyleneamine) with propylene oxide prior to subsequent condensation with ethylene oxide. See also L. Sanders, "Ethoxylation of Fatty Amines," *J. Am. Oil Chem. Soc.*, Vol. 46, (1969), pp. 167-70, which also proposes the same mechanism disclosed in this patent.

U.S. Patent 3,468,904 to Kritchevsky, issued September 23, 1969, discloses that the reaction of fatty acids with hydroxyalkylalkylene polyamines produces objectionable color. Color is reduced by inclusion of borohydrides during the reaction. See also U.S. Patent 3,046,231 to Ernst et al., issued July 24, 1962 (inclusion of borohydrides in the reaction of fatty acids with amino alkane sulfonic acids to prevent color body formation); U.S. Patent 3,687,999 to Kapur et al., issued August 29, 1972 (inclusion of sodium borohydride in the sulfation of ethoxylated long chain aliphatic alcohols to prevent color body formation).

U.S. Patent 3,373,174 to Hammerberg et al., issued March 12, 1968, discloses that the synthesis of fatty amides, especially from unsaturated acids, results in products having undesirable amber color. Color can be reduced by addition of a small amount of a borohydride.

DISCLOSURE OF THE INVENTION

The present invention relates to a process for minimizing color formation during ethoxylation of 2-hydroxyethylamines in the presence of a base catalyst. The 2-hydroxyethylamines for which this process is useful are selected from the group consisting of:

(1) 2-hydroxyethyl monoamines having the formula:



(2) 2-hydroxyethyl diamines having the formula:

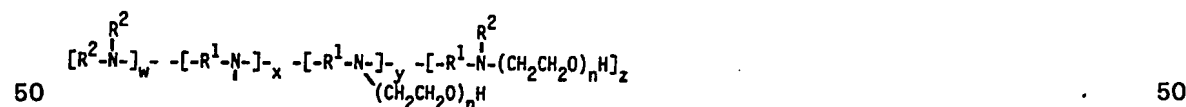


(3) 2-hydroxyethyl polyamines having the formula:

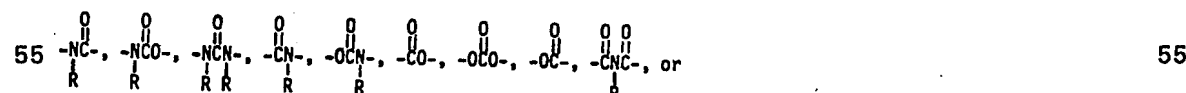


and

(4) 2-hydroxyethyl amine polymers having the general formula:



wherein A¹ is



-O-; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R² is C₁-C₂₂ alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl, the moiety -(CH₂CH₂O)_nH, or two R² together form the moiety -(CH₂)_r-A²-(CH₂)_s-, wherein A² is -O- or -CH₂-, r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; R³ is a substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N

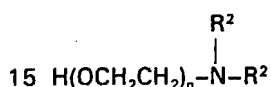
bonds are formed; n is about 1; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2.

The 2-hydroxyethylamine is reacted with ethylene oxide in the presence of a catalytic amount of base and in the presence of an effective amount of a color reducing borohydride. The amount of the ethylene oxide is sufficient to provide at least about 2 moles thereof per each moiety $-(CH_2CH_2O)_nH$ of the 2-hydroxyethylamine.

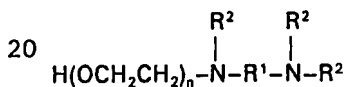
A. 2-hydroxyethylamines

The hydroxyethylamines for which the process of the present invention is useful are selected from the group consisting of:

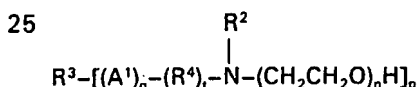
(1) 2-hydroxyethyl monoamines having the formula:



(2) 2-hydroxyethyl diamines having the formula:

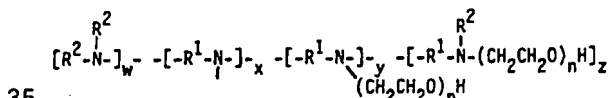


(3) 2-hydroxyethyl polyamines having the formula:

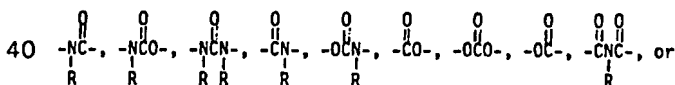


and

(4) 2-hydroxyethyl amine polymers having the general formula:

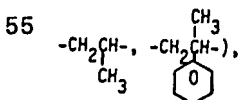



wherein A¹ is

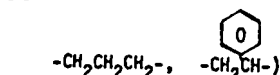


-O-; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R² is C₁-C₂₂ alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl, the moiety $-(CH_2CH_2O)_nH$, or two R² together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A² is -O- or -CH₂-, r is 1 or 2, s is 1 or 2, and r + 2 is 3 or 4; R³ is a substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; n is about 1; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2.

For the diamines and amine polymers, R¹ can be branched (e.g.



cyclic (e.g. ) or most typically linear (e.g. -CH₂CH₂-,

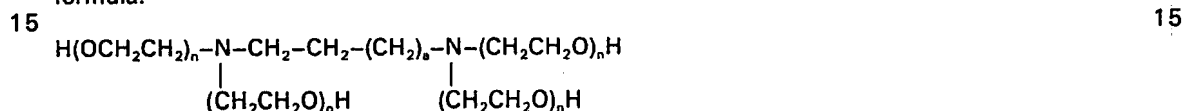


alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R¹ is typically C₂-C₆ alkylene

(e.g., ethylene, propylene, hexamethylene). The process of the present invention is particularly suitable for diamines and amine polymers wherein R_1 is ethylene. These 2-hydroxyethylamines generate significantly greater color during base catalyzed ethoxylation than other 2-hydroxyethylamines.

- 5 In the preceding formulas, each R^2 can be a branched, cyclic or linear C_1 - C_{22} alkyl, hydroxyalkyl, alkenyl, aryl or aralkyl group. A^2 is preferably $-O-$ and $r + s$ is preferably 4. Each R^2 is preferably a C_1 - C_4 alkyl (most preferably methyl) group or the moiety $-(CH_2CH_2O)_nH$. The process of the present invention is particularly useful for those 2-hydroxyethylamines wherein each R^2 is the moiety $-(CH_2CH_2O)_nH$. For the moiety $-(CH_2CH_2O)_nH$, the average value of n is typically 1. However, as a result of lesser or greater ethoxylation of the respective amine to form the 2-hydroxyethylamine, the average value for n can vary somewhat. Usually n is from 0.8 to 1.1. Preferably, n is from 0.95 to 1.0.

Preferred 2-hydroxyethyl diamines used in the process of the present invention have the formula:



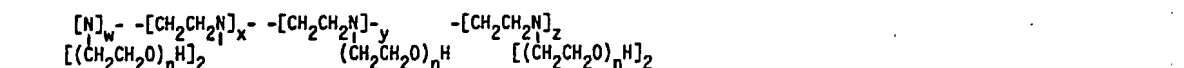
- 20 wherein n is defined as before and a is from 0 to 4.

In the preceding formula for the 2-hydroxyethyl polyamines, R^3 (linear, branched or cyclic) is preferably a substituted C_3 - C_6 alkyl, hydroxyalkyl or aryl group; A^1 is preferably.



- 30 When R^3 is a substituted aryl or alkaryl group, q is preferably 1 and R^4 is preferably C_2 - C_3 alkylene. When R^3 is an alkyl, hydroxyalkyl, or alkenyl group, and when q is 0, R^1 is preferably a C_2 - C_3 oxyalkylene moiety; when q is 1, R^4 is preferably C_2 - C_3 alkylene.

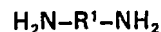
- The 2-hydroxyethyl amine polymers for which the process of the present invention is useful are the 2-hydroxyethyl C_2 - C_3 polyalkyleneamines and polyalkyleneimines. The process of the present invention is particularly useful for 2-hydroxyethyl polyethyleneamines (PEAs) and polyethyleneimines (PEIs). These compounds comprise units having the general formula:



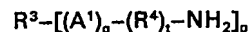
wherein w , x , y , z and n are defined as before.

The 2-hydroxyethyl diamines, polyamines and amine polymers are typically formed by the process of hydroxyethylation of the respective amine. This hydroxyethylation process comprises the steps of:

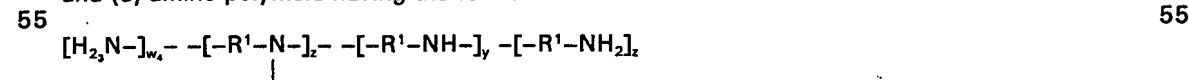
- 45 (a) providing an amine selected from the group consisting of:
(1) diamines having the formula:



- 50 (2) polyamines having the formula:

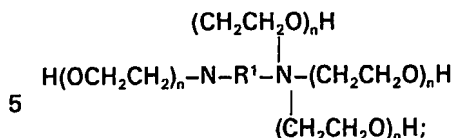


and (3) amine polymers having the formula:

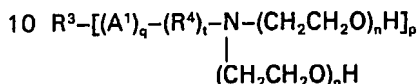


wherein R^1 , R^3 , R^4 , p , q , t , w , x , y and z are defined as before; and

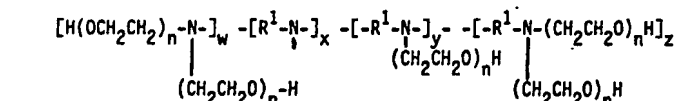
- 60 (b) reacting the amine in the absence of base with an amount of ethylene oxide sufficient to provide a 2-hydroxyethylamine selected from the group consisting of:
(1) 2-hydroxyethyl diamines having the formula:



(2) 2-hydroxyethyl polyamines having the formula;

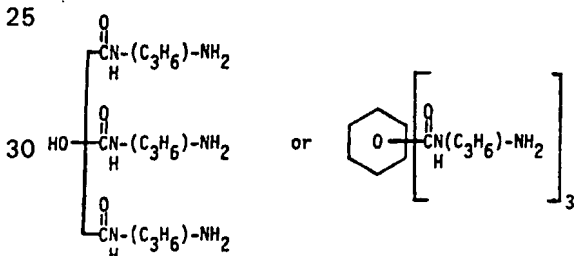


and (3) 2-hydroxyethyl amine polymers having the formula:

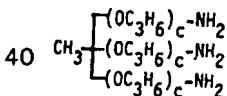


wherein n is about 1.

Suitable polyamines for preparing the respective 2-hydroxyethylamines include polyaminoamides such as:



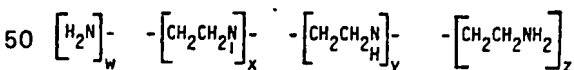
and polyaminopropyleneoxide derivatives such as:



wherein each c is a number of from 2 to about 20.

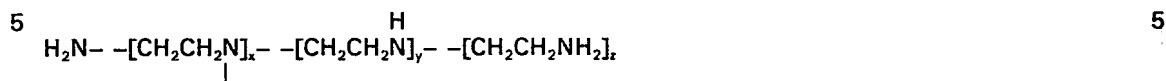
Suitable amine polymers for preparing the respective 2-hydroxyethylamines are the C_2 - C_3 polyalkyleneamines and polyalkyleneimines. Particularly suitable polyalkyleneamines and polyalkyleneimines are the polyethyleneamines (PEAs) and polyethyleneimines (PEIs).

Prior to hydroxyethylation, the PEAs have the following general formula:



wherein $x + y + z$ is from 2 to 9 and w is 0 or 1 (molecular weight of from about 100 to about 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent hydroxyethylation. For preferred PEAs, $x + y + z$ is from about 3 to about 7 (molecular weight of from about 140 to about 310) and most preferably from about 3 to about 4 (molecular weight of from about 140 to about 200). These PEAs can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEAs obtained are ethylene diamine, diethylene triamine, triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines; cyclic amines can also be present in mixtures containing TETA and TEPA. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372 to Dickson, issued May 14, 1957, which describes the preparation of PEAs.

Prior to hydroxyethylation, the PEIs have a molecular weight of at least about 440, which represents at least about 10 units. Preferred PEIs have a molecular weight of from about 600 to about 1800. The polymer backbone of these PEIs can be represented by the general formula:



wherein the sum of x, y and z represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:

15	$-\text{CH}_2\text{CH}_2-\text{NH}_2$	30%	15
	$-\text{CH}_2\text{CH}_2-\text{NH}-$	40%	
	$-\text{CH}_2\text{CH}_2-\text{N}-$	30%	

Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent hydroxyethylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEIs are disclosed in U.S. Patent 2,182,306 to Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746 to Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095 to Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839 to Crowther, issued September 17, 1957; and U.S. Patent 2,553,696 to Wilson, issued May 21, 1951 (all herein incorporated by reference).

B. Reaction of 2-hydroxyethylamine with ethylene oxide in the presence of base

In the process of the present invention, the 2-hydroxyethylamine is reacted with ethylene oxide in the presence of a base catalyst. This process can be a batch reaction, a semi-continuous reaction or a continuous reaction. Typically, the process is carried out as a batch reaction.

If desired, the 2-hydroxyethylamine can be dissolved in a non-polar, unreactive solvent. Examples of solvents which should not be used in the process of the present invention include ketones, aldehydes, alcohols and acidic media. Preferably, the reaction of the 2-hydroxyethylamine with ethylene oxide is carried out in the absence of solvent, i.e. as a neat reaction.

It is important in the process of the present invention that the reaction of the 2-hydroxyethylamine with ethylene oxide be carried out in the presence of base. As used herein, the term "base" refers to those compounds having a pH greater than 7 in water which are capable of catalyzing the reaction of ethylene oxide with the 2-hydroxyethylamine. Also included are those compounds capable of forming base *in situ*. Suitable bases include the alkali metals, the alkali metal hydrides and the alkali metal hydroxides. Examples of such materials include sodium metal, sodium hydride, potassium hydride, sodium hydroxide, and potassium hydroxide. Potassium hydroxide is particularly preferred because it provides a faster reaction rate. Other base catalysts such as sodium carbonate, sodium bicarbonate and calcium oxide can also be used.

The base is used in an amount which is effective to catalyze the reaction of the 2-hydroxyethylamine with the ethylene oxide. What is a "catalytic amount" can depend on various factors. These factors include the base being used, the particular 2-hydroxyethylamine being ethoxylated, the degree of ethoxylation desired, and the reaction rate to be achieved. A particularly important factor is the number of 2-hydroxyethyl (i.e. $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$) moieties on the particular 2-hydroxyethylamine. Usually, the amount of base used is from about 0.01 to about 100 equivalent percent per 2-hydroxyethyl moiety. Preferably, the amount of base is from about 0.5 to about 5 equivalent percent per 2-hydroxyethyl moiety. For those bases in aqueous solution, e.g., sodium and potassium hydroxide, water is desirably removed from the reaction mixture by heat, by vacuum, or by sparging with an inert gas (e.g. nitrogen), before subsequent ethoxylation. Less than about 0.1% water, and preferably less than about 0.01% water, should be present in the reaction mixture.

The reaction of the 2-hydroxyethylamine with ethylene oxide in the presence of base can be carried out at temperatures and pressures normally employed for the ethoxylation of fatty alcohols. The temperature and pressure conditions should be selected to provide a suitable reaction rate while minimizing color formation. At atmospheric pressure, the reaction can be carried out at a temperature of from about 100° to about 160°C. Preferably, the reaction is carried out at a temperature of from about 100° to about 130°C at atmospheric pressure. At higher pressures, e.g., up to about 60 psi when inert gases are used, somewhat higher

temperatures can be used.

- The ethylene oxide reacted with the 2-hydroxyethylamine is typically used in gaseous form. As such, this gaseous ethylene oxide is normally swept into a reaction vessel containing the 2-hydroxyethylamine at atmospheric pressure to effect the reaction. However, where the reaction is carried out at above atmospheric pressure, the ethylene oxide is preferably diluted with an inert gas such as nitrogen, typically in a volume ratio of 2:1 of ethylene oxide to inert gas. The amount of ethylene oxide used generally depends upon the particular 2-hydroxyethylamine involved and the degree of ethoxylation desired. For 2-hydroxyethylmonoamines, the amount of ethylene oxide used is sufficient to provide at least about 11 moles per moiety $-(CH_2CH_2O)_nH$, and preferably at least about 15 moles per moiety $-(CH_2CH_2O)_nH$, with a typical range of from about 14 to about 34 moles. For 2-hydroxyethyldiamines, the amount of ethylene oxide is sufficient to provide at least about 5 moles thereof per moiety $-(CH_2CH_2O)_nH$, and preferably at least about 11 moles per moiety $-(CH_2CH_2O)_nH$, with a typical range of from about 11 to about 41 moles.
- For the 2-hydroxyethyl PEAs and PEIs, the amount of ethylene oxide should be sufficient to provide at least about 2 moles thereof per moiety $-(CH_2CH_2O)_nH$. Where $y + z$ for the PEAs is 2 or 3, the number of moles per moiety $-(CH_2CH_2O)_nH$ is preferably at least about 5. For the PEAs and for the PEIs having a molecular weight of at least about 600, the number of moles of ethylene oxide per moiety $-(CH_2CH_2O)_nH$ is preferably at least about 11, with a typical range of from about 11 to about 41. For PEIs having a molecular weight of at least about 1800, the number of moles of ethylene oxide per moiety $-(CH_2CH_2O)_nH$ is preferably at least about 23, with a typical range of from 23 to about 41.

B. Color reducing borohydride

- The agent used to minimize color formation during the reaction of the 2-hydroxyethylamines with ethylene oxide in the presence of base is a color reducing borohydride. Suitable borohydrides include the alkali metal and alkaline earth metal borohydrides. Examples of suitable alkaline earth metal borohydrides are magnesium borohydride, calcium borohydride, barium borohydride and strontium borohydride. Examples of suitable alkali metal borohydrides are lithium borohydride, sodium borohydride and potassium borohydride. Sodium and potassium borohydride are preferred in the process of the present invention, with potassium borohydride being especially preferred due to its greater solubility in the ethoxylated amine which is formed during the reaction.

- The color reducing borohydride is used in an amount effective to minimize color formation during reaction of the 2-hydroxyethylamine with ethylene oxide in the presence of base. What is "an effective amount" can depend on a variety of factors. Particularly important factors are the borohydride used, the solubility of the borohydride in the ethoxylated amine which is formed during the reaction, and the particular 2-hydroxyethylamine which is ethoxylated. Usually, relatively small amounts of borohydride are used due to its limited solubility in the ethoxylated amine which is formed during the reaction. Typically, use of from about 0.01% to about 0.3% borohydride by weight of the ethoxylated amine which is formed during the reaction is effective to minimize color formation. Preferably, the borohydride is used at from about 0.01 to about 0.1% by weight.

- The borohydride can be included at various points in the process of the present invention. For example, the borohydride can be included in the reaction mixture containing the 2-hydroxyethylamine before the base catalyst is added, or preferably is included after the base catalyst is added. Where the base catalyst is a hydroxide, the borohydride is preferably added to the 2-hydroxyethylamine after water is removed. Quantities of the borohydride can also be metered out at various times during the reaction of the 2-hydroxyethylamine with ethylene oxide. Such a method permits greater amount of borohydride to be used to minimize color formation.

- After the reaction of the 2-hydroxyethylamine with ethylene oxide in the presence of base and in the presence of the color reducing borohydride, it is desirable to neutralize the base with a suitable acid such as hydrochloric acid. The ethoxylated amine formed can be used as is, or can be converted to an aqueous solution which typically contains from about 60 to about 80% by weight of the ethoxylated amine. If desired, additional color reducing borohydride can be added to the ethoxylated amine or to the aqueous solution thereof to further reduce color. To avoid excessive hydrogen gas evolution during storage, it is desirable to heat treat (e.g. at 80°C) the ethoxylated amine or aqueous solution thereof to reduce the amount of borohydride still present.

- Specific Embodiments for Minimizing Color Formation During the Ethoxylation of Tetraethylenepentaamine (TEPA) in the Presence of Base by Inclusion of Sodium Borohydride.*

The following embodiments are used to illustrate the minimization of color formation during ethoxylation of TEPA in the presence of base by including sodium borohydride:

Embodiment I

- TEPA (M.W. 189, 14.2 g., 0.075 moles) was placed in a nominally dry flask and dried by

stirring for 1.7 hours at 110°–120°C under a vacuum. The vacuum was released by drawing ethylene oxide (EO) from a prepurged trap connected to a supply tank. Once the flask was filled with EO, an outlet stopcock was carefully opened to a trap connected to an exhaust bubbler. After 1.3 hrs. of stirring at 104°–117°C, 21.0 g of EO has been added to give a calculated degree of ethoxylation of 0.9. The reaction mixture was cooled while being swept with nitrogen and 1.8 g (0.013 moles) of freshly prepared 40% KOH solution was added. Water was removed by stirring at 120°C under an aspirator vacuum for 1.1 hrs. The vacuum was released by drawing nitrogen into the flask. Once the flask was filled, an outlet adapter was removed and 0.2 g. (0.0053 moles) of NaBH₄ was added while the reaction mixture was swept with nitrogen. EO was then added under atmospheric pressure with stirring at 111°–134°C. After 8.5 hrs., a total of 366 g. (8.3 moles) of EO had been added to give a calculated total degree of ethoxylation of 15.8. The ethoxylated TEPA was a medium brown liquid which cooled to a dark tan waxy solid.

15 Embodiment II

By a procedure similar to that of Embodiment I, dried TEPA (M.W. 189, 14.0 g., 0.074 moles) was hydroxyethylated with EO at 100°–106°C with stirring. After 2 hours, 22.3 g. (0.51 moles) of EO had been added for a degree of ethoxylation of 0.97. After the reaction mixture had cooled somewhat, and while being swept with nitrogen, 1.8 g (0.013 moles) of freshly prepared 40% KOH solution was added. Immediately thereafter, 0.2 g (0.0053 moles) of NaBH₄ was added. Water was removed by stirring at 102°–110°C under an aspirator vacuum for 0.5 hrs., then under a pump vacuum for 0.5 hrs. The vacuum was released by drawing nitrogen into the flask until filled. An additional 0.4 g. (0.01 moles) of NaBH₄ was added with stirring. EO was then added under atmospheric pressure with stirring at 109°–117°C. After 2.25 hrs., 22.9 g. (0.52 moles) of EO had been added for a calculated degree of ethoxylation of 1.98. Since the color of this reaction mixture had darkened, an additional 0.19 g. (0.005 moles) of NaBH₄ was added. Ethoxylation was then resumed at 112°–121°C with stirring. After a total of 12.25 hrs., a total of 275 g. (6.25 moles) of EO had been added to give a calculated degree of ethoxylation of 12.05. The ethoxylated TEPA was a clear dark amber viscous gel (some solid NaBH₄ present) which solidified to a waxy, slightly jellied solid.

CLAIMS

1. A process for minimizing color formation during ethoxylation of 2-hydroxyethylamines in the presence of a base catalyst, which comprises the steps of:

(a) providing a 2-hydroxyethylamine selected from the group consisting of:

(1) 2-hydroxyethyl monoamines having the formula:



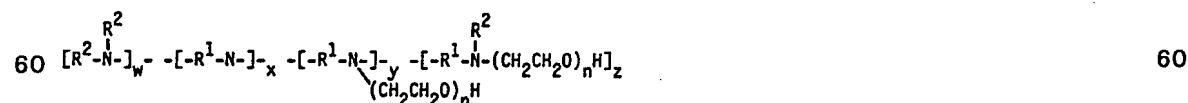
(2) 2-hydroxyethyl diamines having the formula:



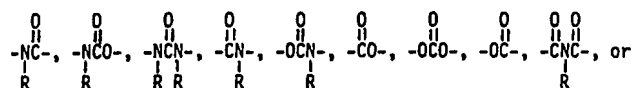
(3) 2-hydroxyethyl polyamines having the formula:



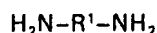
and
(4) 2 hydroxyethyl amine polymers having the general formula:



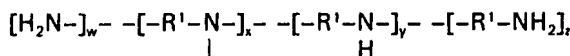
wherein A¹ is



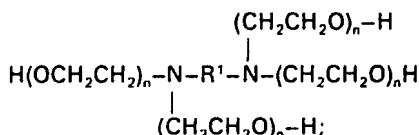
- 5
-O-; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R² is C₁-C₂₂ alkyl, hydroxyalkyl, alkenyl, aryl or aralkyl, the moiety -(CH₂CH₂O)_nH, or two R² together form the moiety
10 -(CH₂)_r-A²-(CH₂)_s-, wherein A² is -O- or -CH₂-, r is 1 or 2, s is 1 or 2, and r + 2 is 3 or 4; R³ is a substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; n is about 1; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is
15 1 when q is 1; w is 1 or 0; x + y + z is at least 2; and
(b) reacting ethylene oxide with the 2-hydroxyethylamine in the presence of a catalytic amount of base and in the presence of an effective amount of a color reducing borohydride, the amount of ethylene oxide being sufficient to provide at least about 2 moles thereof per each moiety -(CH₂CH₂O)_nH of the 2-hydroxyethylamine.
20 2. A process according to Claim 1 wherein each R² is the moiety -(CH₂CH₂O)_nH.
3. A process according to Claim 2 wherein R¹ is ethylene.
4. A process according to Claim 3 wherein the borohydride is selected from the group consisting of sodium and potassium borohydride.
5. A process according to Claim 4 wherein the amount of borohydride is from about 0.01 to
25 about 0.3% by weight.
6. A process according to Claim 5 wherein the amount of ethylene oxide is at least 11 moles per each moiety -(CH₂CH₂O)_nH.
7. A process according to Claim 6 wherein said reaction step (b) is carried out in the absence of solvent.
30 8. A process according to Claim 7 wherein the base is selected from the group consisting of sodium metal, sodium hydride, potassium hydride, sodium hydroxide and potassium hydroxide.
9. A process according to Claim 8 wherein said reaction step (b) is carried out at a temperature of from about 100° to about 160°C at atmospheric pressure.
10. A process for minimizing the color of ethoxylated amines, which comprises the steps of:
35 (a) providing an amine selected from the group consisting of:
(1) diamines having the formula:



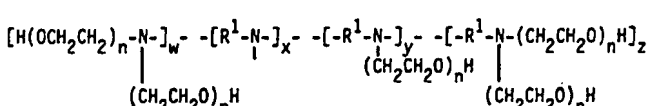
- 40 and; (2) amine polymers having the formula:



- 45 wherein R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; w is 0 or 1; x + y + z is at least 2;
(b) reacting the amine in the absence of base with an amount of ethylene oxide sufficient to provide a 2-hydroxyethylamine selected from the group consisting of:
50 (1) 2-hydroxyethyl diamines having the formula:



- and (2) 2-hydroxyethyl amine polymers having the formula:



- 65 wherein n is about 1; and

(c) reacting the 2-hydroxyethylamine with ethylene oxide in the presence of a catalytic amount of base and in the presence of an effective amount of a color reducing borohydride, the amount of ethylene oxide being sufficient to provide at least about 2 moles thereof per each moiety $-(CH_2CH_2O)_nH$ of the 2-hydroxyethylamine.

- 5 11. A process according to Claim 10 wherein R^1 is ethylene. 5
12. A process according to Claim 11 wherein the borohydride is selected from the group consisting of sodium and potassium borohydride.
13. A process according to Claim 12 wherein the amount of borohydride is from about 0.01% to about 0.1% by weight.
- 10 14. A process according to Claim 13 wherein the amount of ethylene oxide is at least 11 10 moles per each moiety $-(CH_2CH_2O)_nH$.
- 15 15. A process according to Claim 14 wherein said reaction step (b) is carried out in the absence of solvent.
16. A process according to Claim 15 wherein the base is selected from the group consisting of sodium metal, sodium hydride, potassium hydride, sodium hydroxide and potassium hydroxide. 15
17. A process according to Claim 16 wherein n is from 0.8 to 1.1.

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